



## Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact [support@jstor.org](mailto:support@jstor.org).

*Analysis 3.* In this analysis, in which I was prevented from determining the carbon, 0.1537 of bi-sulphide of carbon gave 0.9461 of sulphate of baryta, corresponding to 84.5 per cent of sulphur.

The mixture of asbestos and peroxide of lead employed was of that which had already been used in the preceding analyses, and may possibly have contained a trace of undecomposed sulphate of lead, as the per cent of sulphur found in this case is 0.3 per cent above, while in the preceding analyses it was a fraction below the theoretical quantity. Trusting, however, that the results already obtained will be deemed sufficient to show the method to be a good one, I have not thought it advisable at this time to further repeat the analysis of this substance. I may here state that I have already applied the process in the analysis of bodies containing hydrogen, and have obtained satisfactory results which will soon be published.

The important advantage thus gained of being able to determine the different elements from the same portion of substance, considering also the simplicity of the process, can hardly fail, I think, to secure for this the preference over the older methods.

---

**Five hundred and forty-ninth Meeting.**

March 28, 1865. — SPECIAL MEETING.

The PRESIDENT in the chair.

Professor Gibbs presented the following paper.

*Observations on Crystals and Precipitates in Blowpipe Beads.*

By GEORGE H. EMERSON.

Believing that the subject of this article is so far novel, at least, as not to have been brought into general notice through the press, I have thought it of sufficient interest to merit publication.

While studying, a few months since, the blowpipe behavior of the alkaline earths, I noticed that the opacity produced by "flaming," or exposing to an intermittent heat, a borax bead sufficiently saturated with one of the earths, was often only partial, — a variable portion of the bead becoming opaque white, while the remainder was perfectly transparent. The extent of the opacity seemed dependent on the duration of the heat. Moreover, when nearly the whole surface was obscured,

the interior was transparent; for, upon carefully removing the external part of the bead, a clear, vitreous nucleus was disclosed; but beads exposed to longer heat, when broken showed no trace of this vitreous interior.

But just beginning the study of Chemistry, I was wholly unacquainted with the phenomena of the devitrification of glass, and did not feel well assured, therefore, that crystallization was the cause of this opacity, though it occurred to me at the time that such was probably the case. But if the change produced by flaming was a result of crystallization, then a crystalline structure ought under some circumstances to be discernible; and the density of the crystallized portion could be no obstacle, as I had already ascertained *that* to be variable at the pleasure of the operator, my experiments yielding results of every degree, from a translucent film to complete opacity. Although density of aggregation did not seem to stand in the way, minuteness of crystalline form might be an impediment to investigation. A borax bead charged with lime exhibited a thin, filmy band stretching across the otherwise transparent surface, when slightly heated with a fine-pointed flame; but in this I could find no crystals with a hand lens magnifying fourteen diameters. Magnesia, however, when similarly treated, gave a very different result. The bead became studded with beautiful, needle-like crystals, arranged in tufts, or fascicular bunches, and visible even to the naked eye. Several trials with the same base confirmed the fact of crystallization, and showed a surprising uniformity of crystalline form. But was this form, seemingly constant, a character whereby to recognize the earth, or would other members of the group likewise exhibit it, if properly dealt with? for the experiments with magnesia had taught me that crystals were not always obtained by flaming, an amorphous cloud being sometimes the only result. I reverted to lime; but with no success. I could get no crystals. Next, I tried baryta. The first trial of slight flaming yielded crystals, of which the hexagonal and rectangular outline could be easily seen without a glass. Sometimes a third shape was visible, looking something like an hour-glass; but these forms seemed to be constant, and there was nothing in the beads in the least resembling the magnesia crystals. Strontia, similarly treated, yielded transparent crystals of a plumose character.

Three members of the group, then, had yielded crystals with borax; and crystals possessing quite well-marked distinctive characters. Lime

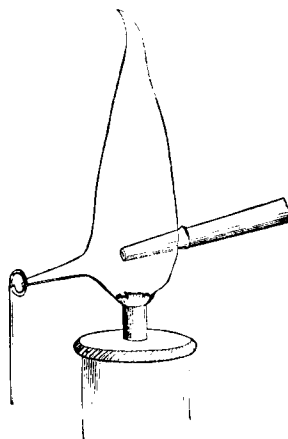
did not crystallize, its opacity, as seen when magnified two hundred diameters, being due to a dense aggregation of exceedingly minute bubbles. Upon treatment with microcosmic salt, lime and magnesia gave, with very slight flaming, nebulous films; that of the former being resolvable into a multitude of spicular crystals, when magnified four hundred times; and the latter into rectangular crystalline forms, in most cases, very nearly square. With the same flux, baryta gave hexagonal crystals, discernible by the naked eye; and which, when not rendered too opaque by prolonged flaming, viewed under the microscope, resembled the common stellate form of snow crystals. Strontia produced equally conspicuous crystals, but of a rectangular form, the length being twice or three times the breadth.

Several experiments with each of the bases just named, in both fluxes, showing no variation in crystalline form from those I had already observed, although in every instance I submitted the result of my trials to microscopic examination, rarely using a less magnifying power than eighty diameters, I passed on to such of the other earths and metallic oxides as were within my reach, of which a list will be found upon page 481.

Before describing in detail the phenomena produced by flaming with these several substances, a few words in reference to the methods pursued may not be unacceptable; premising, however, that these statements, together with all included in these pages, are not predicated upon sufficiently numerous experiments to be regarded as authoritative; and that they are offered rather as suggestions to persons better fitted, and with more ample leisure and opportunity than the author, to follow out the subject exhaustively.

The loop of platinum wire should be about one eighth of an inch in diameter, and quite circular, in order to give as uniform convexity to the surface of the bead as possible. Two turns of the wire are better than one where microcosmic salt is used, on account of the greater fluidity of this flux than borax. The bead should not be much over one twentieth of an inch thick at least, where examination by a high magnifying power is desirable. Crystallization is best produced by thrusting the tip of the blowpipe well into the flame of the lamp, until a fine-pointed jet of flame, less than an inch in length, is obtained; then expose a small portion of the bead, close to the edge, (see diagram,) for an instant to its action, until the part so exposed,

and the wire immediately adjacent, become of a dull red heat, when the bead should be at once withdrawn, and examined with the lens. It may be necessary to repeat this operation several times before crystals are obtained: but the bead should always be cool when heat is applied. Often an amorphous cloud will be the only result, even of repeated trials, although the substance employed is quite easily crystallizable; and this is especially apt to be the case when the bead is too highly charged, or when heated too long, the suspended matter being then so rapidly precipitated as to prevent crystallization. The bead should in such cases be subjected to the action of a powerful flame till perfect transparency is obtained, and, if the first mentioned be the difficulty, a little more of the flux added before again flaming.



It seems to make little difference with the earths whether the glass containing them be prepared in the oxidating or reducing flame, previous to flaming, though they are most readily dissolved at the point of greatest heat; but the oxides of the non-volatile metals give the best results when the bead is charged in the oxidating, and, after cooling, subjected to the action of a fine-pointed reducing flame. One advantage of using this small fine-pointed flame is, that only a portion of the bead is subjected to the reducing influence; and as the heat is maintained but an instant, the portion of the glass fused is not only circumscribed, but superficial, so that the reaction takes place where it can easily be observed. Moreover, a devitrifying action goes on, at the same time, in the unfused but reheated portion of the bead.\* I shall use the term "intermittent flame" to distinguish the ordinary process of flaming from that just described.

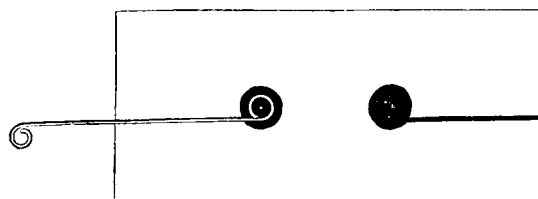
The amount of the substance used varies, of course, with the subject of the experiment, although the formation of striae in the glass,

---

\* As the method of treating beads just described in the text promises to be of value, in certain of its applications, in the arts, as well as of scientific interest, *the author intends to secure such applications by patent*, after having made some additional experiments.

which are easily seen with the lens, when the bead is not so highly colored as to render them invisible, is in general an indication that the proper point of saturation has been reached.

In examinations with a compound microscope, I have found cork slides, two and one fourth inches long, one inch broad, and one sixth of an inch thick, very convenient. Two perforations are made through the cork, somewhat larger than the beads, which are placed in the centre, and easily retained in position by sinking the wire used for a handle into slits in the cork prepared to receive them. (See diagram.)



This adjustment holds the bead steadily, and, combined with the flexibility of the wire, permits any part of the convex surface to be brought into field, which is very important, as the crystals are very frequently formed only close to the margin.

In photographing the crystallizations, the beads being transparent, and transmitted light employed, the solar rays were reflected from the surface of a *concave* mirror, their power being diminished by the interposition of a piece of ground glass between the mirror and the bead; the curved surface of the bead rendering the illumination by the plane mirror very unsatisfactory.

In regard to the ensuing descriptions of the crystalline reactions of the substances dealt with, although the phenomena differ very perceptibly to the eye of the microscopic observer, yet I have found it exceedingly difficult to convey verbally any exact conception of their differences; and have, therefore, contented myself with roughly sketching the most prominent features, feeling assured that a few easily made experiments will, to persons interested, be in every case far more satisfactory than any written description. On the next page will be found a list of the substances experimented upon.

I cannot conclude these introductory remarks without expressing my obligations to Professor Josiah P. Cooke, who has kindly furnished me with many of the rarer substances experimented with, and to my

friend, Mr. A. E. Verrill, assistant in the Museum of Comparative Zoölogy, to whom I am indebted for the photographs from which the plate was taken, and who, in the midst of pressing occupations, has accomplished for me what professional photographers would not undertake.

## LIST OF SUBSTANCES EXPERIMENTED UPON.

Baryta, . . . . .	(Ba O)	Tin, Binoxide of, . . . .	(Sn O <sub>2</sub> )
Strontia, . . . . .	(Sr O)	Silver, Oxide of, . . . .	(Ag O)
Lime, . . . . .	(Ca O)	Copper, " " . . . .	(Cu O)
Magnesia, . . . . .	(Mg O)	Nickel, " " . . . .	(Ni O)
Alumina, . . . . .	(Al <sub>2</sub> O <sub>3</sub> )	Cobalt, " " . . . .	(Co O)
Glucina, . . . . .	(Gl <sub>2</sub> O <sub>3</sub> )	Manganese, Red Oxide of, .	(Mn <sub>2</sub> O <sub>4</sub> )
Zirconia, . . . . .	(Zr <sub>2</sub> O <sub>3</sub> )	Iron, Sesquioxide of, . .	(Fe <sub>2</sub> O <sub>3</sub> )
Zinc, Oxide of, . . . .	(Zn O)	Uranium, Sesquioxide of, .	(U <sub>2</sub> O <sub>3</sub> )
Cadmium, Oxide of, . .	(Cd O)	Chromium, Sesquioxide of, .	(Cr <sub>2</sub> O <sub>3</sub> )
Lead, " " . . . . .	(Pb O)	Tungstic Acid, . . . .	(W O <sub>3</sub> )
Bismuth, Teroxide of, .	(Bi O <sub>3</sub> )	Titanic Acid . . . . .	(Ti O <sub>2</sub> )
Antimony, " " . . . .	(Sb O <sub>3</sub> )	Molybdic Acid, . . . .	(Mo O <sub>3</sub> )
Arsenic (Arsenious Acid) .	(As O <sub>3</sub> )		

*Supplement.*

Niobic Acid . . . . .	(Nb <sub>2</sub> O <sub>5</sub> )	Tellurium	
Selenium		Cerium, Protoxide of, . . .	(Ce O)

*Baryta*.—Baryta is dissolved in borax in large quantities before a precipitate is obtained.\* When carefully flamed, opaque, milk-white crystals of a hexagonal, and also of an hourglass shape, are formed (see Plate, Figs. 1 and 2), often distinctly visible even to the naked eye. There are likewise, sometimes, aggregations of rectangular crystals. In what corresponds to the terminal, or basal planes of the hourglass-shaped crystal, a hexagonal outline may be observed in the one delineated in the plate (see Fig. 2); but, rarely having obtained so large and perfect crystals of this form as the one photographed, I am unable to say how constant this feature may be.

With microcosmic salt, slight flaming produces beautiful hexagonal, stellate crystals, not opaque, at least in their inception, and exhibiting a structure resembling some of the commonly depicted forms of snow-flake crystals. Accompanying these I have noticed a rectangular

\* As a matter of convenience, I use the term "precipitate" to designate the crystalline or other aggregation, produced by the flaming process within or upon the surface of the bead.

crystal. Further flaming renders these crystals opaque white. They are sometimes produced on cooling merely, without submitting the bead to the flaming process.

*Strontia.* — Strontia, with borax, yields plumose crystallizations, more or less translucent, according to the state of saturation of the glass, and the amount of flaming; and which are made up of slender, bladed crystals, sometimes arranged around a common centre in nearly circular disks.

With microcosmic salt, slight flaming gives to the surface of the bead a peculiar speckled aspect, due to the formation of oblong, rectangular crystals, varying in size, being often large enough to be made out without using a lens (see Plate, Fig. 3); but never possessing such well-defined angles as the crystallizations of baryta. (See Plate, Fig. 3.) This is a better reaction than that with borax.

Mixed with an equal quantity of baryta, in the same flux, a precipitate is instantaneously produced by flaming, made up of microscopic spiculæ, sometimes asteriated. The most superficial observation would not, however, confound this reaction with that obtainable from the earths separately.

*Lime.* — Lime, with borax, yields on slight flaming a thin, filmy precipitate, often in the form of a band stretching across the surface of the bead; but in which I have never been able to detect any crystals, the element of opacity being a dense aggregation of colorless, microscopic globules, or bubbles.

Mixed with an equal quantity of magnesia, I have been unable to obtain any different reaction from that just described.

With microcosmic salt, delicate flaming produces a slight precipitate, which, when highly magnified, is seen to be made up of exceedingly minute spiculæ, closely aggregated.

*Magnesia.* — With borax, magnesia yields quite readily elegant, acicular crystals, almost invariably united in tufts, or sheaf-like bunches. (See Plate, Fig. 4.)

With microcosmic salt, microscopically small crystals are produced by slight flaming, sometimes possessing a stellate form, and sometimes being rectangles approaching the square. The reaction with borax, I regard as by far the most decisive.

*Alumina.* — With borax, alumina dissolves to a limpid glass, which is not rendered opaque by saturation or flaming. When more of the earth is present than can be dissolved by the flux, prolonged blowing



produces a white, vitreous-looking exudation at the margin of the bead, which is hard enough to scratch glass, and is not easily soluble in borax. Keeping the bead a long time at a high temperature produces the same effect, even when the glass is not saturated; and the same thing occurs when this earth is treated with microcosmic salt.

With microcosmic salt, patient flaming is rewarded by a very slight precipitate, consisting of an immense number of exceedingly minute, asteriated crystals, partaking of the snow-flake character, but not nearly so well defined and symmetrical as the crystallizations of baryta with the same flux.

In borax, mixed with an equal quantity of lime, I have obtained crystals; but of a very irregular form, and unfinished appearance. It should be borne in mind, however, that I have not been able to crystallize either of these earths *alone* in borax.

*Glucina.* — With borax, an exudation, similar to that noticed with alumina, takes place upon long heating. Flaming produces a precipitate composed of colorless globules or bubbles. Mixed with an equal quantity of lime, a similar precipitate is obtained.

With microcosmic salt, upon flaming, the surface of the bead becomes studded with crystals, but so minute as to require a high magnifying power to discern their form. They are generally rather slender, solitary, oblong figures; but quite often cruciform, and sometimes irregularly assembled.

*Zirconia.* — In borax, the intermittent flame causes a crystalline precipitate; but the individual forms are too minute to be distinguished, when magnified four hundred diameters. Long blowing produces the exudation observed with the two preceding earths. Addition of lime, in very considerable quantity, causes a very decided precipitate upon flaming, consisting of bubbles. The zircon, from which the earth used was prepared, gave a similar precipitate to that last named, but much less dense.

With microcosmic salt, flaming is followed by the formation of an indistinct, crystalline film.

*Zinc.* — Oxide of zinc, with borax, yields, in the intermittent flame, acicular crystals, arranged in tufts, asteriated, and sometimes arborescent. These crystals resemble those of magnesia in the same flux, except that I have not observed either the stellate or arborescent arrangement with the latter. In the reducing flame a bright metallic precipitate, flesh-colored to brassy, is easily obtained, after adding oxide

of copper, thorough fusion in the outer flame, and refrigeration of the bead.

With microcosmic salt, crystals are formed, in the intermittent flame, which I am inclined to regard as flattened octohedrons.

*Cadmium.* — With borax, in the intermittent flame, oxide of cadmium gives crystals much like those of zinc and magnesia, except that the tendency to a stellar arrangement is more marked than with either of the last-mentioned substances. In the reducing flame, oxide of copper being previously added, the precipitate is similar to that observed with zinc, but not so brassy, and bordered, moreover, on the edge from the flame, by iridescent bands, which I have not observed with zinc.

In microcosmic salt, it crystallizes in rectangles, one diameter being two or three times greater than the other. The crystals are quite minute, and, generally, transparent.

*Lead.* — With borax, and treated in the intermittent flame, litharge gives a precipitate consisting of microscopically minute spheres, darker than the globules mentioned as occurring with some of the earths; and associated with which I have noticed a few prismatic crystals, so small as to be scarcely distinguishable, even when magnified four hundred diameters. Slightly heated in the reducing flame, a dark-gray, lustreless, amorphous precipitate appears on the surface of the bead.

With microcosmic salt, the phenomena, with the intermittent flame, are much the same as when borax is employed, except that, in most instances, the precipitate is crystalline rather than globular.

*Bismuth.* — Oxide of bismuth does not crystallize, in the intermittent flame, with borax, but yields globules like those of lead. Touched with the reducing flame, I have observed a slight, amorphous precipitate on the surface of the glass; but not nearly so dark, or distinct, as that of lead. With litharge, a partially metallic precipitate is obtained. With oxide of copper, the precipitate resembles that of zinc, though, perhaps, somewhat less lustrous.

With microcosmic salt, it crystallizes in very small, square, transparent disks, when treated in the intermittent flame. A considerable number of globules, like those observed in the borax beads, accompany the crystals.

*Antimony.* — In borax, teroxide of antimony yields no precipitate, either with the intermittent or reducing flame, although they both produce a peculiar corrugation on the surface of the glass. Addition of

litharge is followed by the appearance of an apparently insoluble substance, in the glass, which renders it opaque without devitrification taking place; but the reducing flame does not produce a precipitate in a bead thus treated. When teroxide of antimony is added, in considerable quantity, to a bead colored dark blue with oxide of copper, and just removed from the oxidating flame, it is at once taken up by the still fluid glass, in which an amorphous, red precipitate — apparently sub-oxide of copper — is immediately formed. When the copper bead is a very dark, nearly opaque, blue, addition of much teroxide of antimony converts it, *after fusion in the outer flame*, into a parti-colored enamel, in which red and yellow predominate; and the bead, upon cooling, loses its uniform convexity of outline, the surface becoming very irregular. Treated in the reducing flame, a rather indistinct, dull-gray looking precipitate is then obtained. When much less teroxide of antimony is present, the precipitate is not unlike that of zinc, though it is, in most cases, accompanied by a red border of sub-oxide of copper, which I have not noticed in the zinc beads.

With microcosmic salt, I have noticed an amorphous precipitate on the surface of the glass, when treated in the reducing flame, which was, in one case, accompanied by solitary, needle-like crystals, distinguishable by the lens.

*Arsenic.* — With the intermittent flame, I have not obtained crystals in either flux.

Addition of arsenious acid to a hot borax bead, colored dark blue with oxide of copper, is immediately succeeded by the formation of a precipitate similar to that just described under the head of antimony; but in no case, however large be the quantity of arsenious acid added, does the bead lose its form, or assume the colors of the antimony enamel, after being reheated in the outer flame. The precipitate in the reducing flame is principally sub-oxide of copper, accompanied sometimes, however, by brassy-looking, metallic particles. With sesquioxide of iron, there is a rather scanty precipitate, in the reducing flame, in color and lustre not unlike metallic arsenic.

*Tin.* — In borax, bin oxide of tin yields a very slight, filmy precipitate, in the intermittent flame, made up of exceedingly transparent, but very indefinitely shaped crystals, which, viewed under the microscope, bring forcibly to mind a pellicle of recently formed ice floating in clear water, the corrugations of whose surface alone serve to distinguish it from the fluid on which it rests.

With oxide of copper, and treated in the reducing flame, the precipitate closely resembles that of zinc under the same circumstances.

With microcosmic salt, I have observed no crystallization.

*Silver.* — Oxide of silver, fused with borax in the outer flame, to a clear glass, and treated with the reducing flame, gives a yellowish precipitate of very minute crystals, of which the form appears to be octohedral; and with microcosmic salt, the reaction is similar.

Addition of considerable oxide of silver to a bead containing litharge renders it opaque, and of an oil-yellow color. Treated in the reducing flame, there is a precipitate of what appears to be metallic silver, in minute globules and irregularly shaped masses. The part of the bead acted upon likewise becomes straw-colored, and slightly iridescent. When oxide of copper is substituted for litharge, the bead becomes opaque, and of a light greenish-blue color. Touched with the reducing flame, the part within its influence changes to a very beautiful pale blue, bordered by bands of a somewhat cupreous shade, and enriched by a fine play of colors. A precipitate resembling metallic silver frequently accompanies this reaction. With oxide of nickel, in the outer flame, a grayish-brown, streaked enamel is produced. The reaction with the reducing flame slightly resembles that with copper; but the bands around the part heated are very light, — almost white, in fact, — and the delicate pale blue of the copper reaction is entirely wanting. With teroxide of antimony, in the reducing flame, there is a metallic precipitate. Addition of litharge to the silver-copper and silver-nickel beads, and treatment with the reducing flame, produces a metallic precipitate, in the form of globules distinguishable with the lens.

*Copper.* — Oxide of copper, with borax, and treated as just described under silver, yields a metallic precipitate, which is somewhat increased by addition of litharge.

With microcosmic salt, there is a similar precipitate, accompanied sometimes by the formation of sub-oxide of copper.

By means of the reaction with borax, I have detected copper — obtaining a metallic cupreous precipitate, in an iron pyrites, said to contain but two or three per cent of that metal; and where the proportion of copper was so small, that it did not affect the characteristic iron-yellow of the glass when heated in the outer flame.

*Nickel.* — With borax, oxide of nickel gives a gray, metallic precipitate, when heated in the reducing flame. Addition of litharge renders

the precipitate somewhat globular. Arsenious acid does not seem materially to affect the character of the precipitate; nor do the sesquioxides of iron and chromium, and the red oxide of manganese. With equal parts of the oxides of nickel and copper, the color of the precipitate indicates the presence of both metals, in some parts the cupreous, and in others the nickelic hue prevailing. Where the oxide of copper is very considerably in excess of the nickel, the precipitate has still a decidedly grayish cast; but when the latter oxide is in excess, the presence of copper is scarcely perceptible, aside from the blue color it imparts to the glass.

With microcosmic salt, the reactions are similar to those described with borax; but not so easily obtained, owing, perhaps, to the greater fluidity of glasses made with that flux.\*

*Cobalt.*—With borax, oxide of cobalt, in the reducing flame, gives a gray metallic precipitate, not distinguishable from that of nickel. Arsenious acid causes a larger precipitate, but does not affect its appearance. Sesquioxide of iron seems to promote the precipitation of the cobalt. With an equal amount of oxide of copper, the precipitate is cupreous, inclining to gray, the latter shade being best recognized by comparison with a pure copper precipitate.

*Manganese.*—In a borax bead, highly colored by oxide of manganese, but still translucent, a scanty dark-colored precipitate is obtained in the reducing flame; but this precipitate is not metallic, and seems to be *within* the glass rather than on its surface. Lime seems to hasten this reaction; and after adding this substance I have noticed a crystalline precipitate form upon flaming. The crystals were transparent prisms, quite large, and apparently modified.

With microcosmic salt, in the reducing flame, there is a crystalline precipitate, composed of spiculæ, bearing some resemblance to those of lime, only rather larger and more conspicuous than any I have observed with that earth.

*Iron.*—Sesquioxide of iron, fused with borax, in the outer flame, to a dark, brownish-yellow bead, and then treated with the reducing flame, affords an amorphous precipitate, in streaks and reticulated

---

\* In treating pyritic minerals, they should be carefully roasted before fusion with borax, otherwise a precipitate of sulphide of iron may occur, which somewhat resembles the metallic precipitates of Nickel and Cobalt, and might be mistaken for one of those metals, thereby misleading the operator as to the constitution of the substance under examination.

aggregations, which appear black by transmitted, and grayish-black by reflected light. When the bead saturated with iron is heated for some time in the ordinary *reducing* flame, and, when quite cold, a small portion of its surface exposed for a few seconds to the influence of the small fine-pointed *reducing* flame, the precipitate which forms is apparently metallic. When a bead, nearly opaque with sesquioxide of iron, is thoroughly fused in the outer flame, teroxide of antimony added, and then reheated for a short time in the *same* flame, a gray metallic-looking precipitate forms on the surface, upon cooling. Substituting arsenious acid for antimony, the experiments otherwise being conducted in the manner just described, I have obtained no precipitate whatever. Lime and litharge seem to have but little effect on the iron reaction. Upon adding the red oxide of manganese, I have noticed a dark cloudy precipitate form in the glass, after treating with the reducing flame; but the reaction is very unsatisfactory.

*Uranium.* — With borax, in the *intermittent* flame, sesquioxide of uranium yields a light-colored flocculent-looking precipitate; but no crystals, so far as I have observed. In the reducing flame, the precipitate is very much like that of iron; and addition of sesquioxide of iron, or lime, does not sensibly affect it. Manganese produces, in the reducing flame, the same precipitate that it does with iron.

In microcosmic salt, I have obtained a crystalline precipitate; but the form of the crystals was not determinable, when magnified four hundred diameters. This precipitate formed only after repeated applications of the *reducing* flame. Upon adding sesquioxide of iron, I noticed crystals, in outline like those of strontia, but much smaller than any that I have seen of that earth.

*Chromium.* — Sesquioxide of chromium, fused with borax in the outer, and then treated with an *intermittent inner* flame, yields a glass filled with bubbles which are often microscopic. Reversing the process, viz. first treating with the reducing flame, is followed by the same result. With microcosmic salt, I have not obtained any different reaction. Berzelius alludes to this phenomenon, in his treatise on the blowpipe, stating at the same time his inability to account for it.

*Tungstic Acid.* — With borax, in the reducing flame, tungstic acid readily yields a crystalline precipitate, often bluish at the edges, and slightly iridescent. Under the microscope, this precipitate strikingly resembles the arborescent crystallizations of frost upon window-glass

(see Plate, Fig. 5); and, when viewed by reflected light, it exhibits a frosty lustre. Mixed with an equal quantity of sesquioxide of iron, the tungstic acid reaction is easily obtained, and quite apparent, in a translucent glass; but where the bead is opaque from excess of iron, a slight grayish precipitate only is distinguishable. Silicic acid seems to promote the formation of this precipitate, even when added in large quantities. Equal parts of tungstic acid and oxide of copper give a cupreous precipitate, but decidedly grayish.

With microcosmic salt, the reactions are much the same as with borax; except that in a transparent bead containing a mixture of sesquioxide of iron and tungstic acid I have noticed, besides the arborescent variety, crystals of a hexagonal stellate form, one of the axes being, however, at least one half longer than the others, thus giving to the crystals a distorted aspect.

*Titanic Acid.*—In borax, treated with the reducing flame, titanic acid affords an amorphous, blue precipitate, usually as a band stretching across the surface of the bead. Mixed with equal parts of tungstic acid, in the reducing flame, the reaction of the last-named acid is very apparent, while that of titanic acid might easily be confounded with the blue border mentioned as frequently accompanying the tungstic acid precipitate; though I am inclined to think that the presence of the titanic acid renders the blue color deeper and more distinct. An excess of titanic acid gives a blue band, too well defined to be easily mistaken for any similar appearance of tungstic acid; yet the reaction of the latter is quite apparent, even when the former is three or four times in excess. Mixed with sesquioxide of iron, avoiding an excess of iron, however, the blue titanic acid precipitate is easily obtained and recognized, the glass being still translucent. When the quantity of sesquioxide employed was six or seven times that of the acid, I obtained a very dark iron-gray precipitate, on the surface of an opaque bead. Equal parts of titanic acid and oxide of copper yield a slightly gray copper precipitate.

With microcosmic salt, in the reducing flame, titanic acid gives a transparent, colorless crystalline precipitate.

*Molybdic Acid.*—With borax, in the reducing flame, molybdic acid yields quite easily a lustrous, iridescent metallic precipitate, in color from silver-gray to black, and bordered, on the side remote from the flame, by a brown band. In the portion of the glass not obscured by this precipitate I have noticed transparent hexagonal and rhomboidal

crystals, (see Plate, Fig. 6,) accompanied by very irregularly shaped, but equally transparent, crystalline masses. In mixtures of equal parts of molybdic acid and oxide of copper, the copper precipitate is somewhat inclined to gray. With sesquioxide of iron, there is a black metallic-looking precipitate, not iridescent. When the iron was considerably in excess, the precipitate was slight, and difficultly obtainable. In presence of manganese, the precipitate was quite dense, and simply characteristic of molybdic acid; and such was also the case in mixtures of equal parts of molybdic and tungstic, and molybdic and titanitic acids.

With microcosmic salt, I have obtained a precipitate similar to, but less distinct than, that noticed with borax.

#### CONCLUDING REMARKS.

Beads, at a certain point of saturation, will become wholly or partially opaque upon cooling; and, under such circumstances, well-defined crystalline forms are sometimes produced; but they are generally obscured by the increase of the devitrified portion of the glass, during the process of cooling. In two or three instances, however, while experimenting with baryta, I have observed distinctly marked hexagonal crystals form *beneath* the surface of the glass (when obtained by the reheating or flaming process, the crystallizations are quite close to the surface), as it cooled after complete fusion, prior to flaming, without any further devitrification taking place; and the crystals of Fig. 1 of the plate are examples of this kind.

Wherever mention is made in the foregoing pages of treatment with the "reducing flame," the short, fine-pointed flame of the diagram, described in the commencement, is intended, except in one or two cases, where the "whole surface of the bead" is spoken of as being acted on by the reducing flame; and *previous fusion in the oxidating flame, and cooling of the glass, is always presupposed*, unless a different method of procedure is explicitly stated. An "intermittent reducing flame" is also alluded to, and by this is meant repeated applications of the fine jet of flame, time being allowed between each application for the bead to cool. This method will often insure a precipitate where a single heat would altogether fail, which is especially apt to be the case in glasses not very highly charged with the subject of experiment; for, it must be borne in mind, it will not do to heat the bead too long at any one time, when a precipitate by reduction is desired, as the precipitate



ordinarily forms at or near the margin of the red-hot portion of the glass, the tendency seemingly being to aggregate away from the point of greatest heat, and in a matrix which has not assumed the fluid condition. In consequence of this tendency, if the heat be too long continued—which may be known by the reddening of the whole or greater part of the surface of the bead—the precipitate, especially when scanty, is driven completely off the glass and thrown upon the wire loop, where it is often invisible, besides exercising, if in the metallic state, a damaging influence on the wire itself. Frequently the precipitate is in the form of a narrow, crescent-shaped band, at the edge of the heated portion of the glass; and repeated cautious applications of the flame will generally produce a repetition of these bands; thus rendering quite distinct what otherwise might scarcely have been visible.

Where the precipitate is metallic, translucency of the glass is not important, and, unless microscopic study is intended, rotundity of the bead is not objectionable; on the contrary, within certain limits, is preferable, on account of its being more slowly heated, and thus allowing a more prolonged action of the flame.

In reference to the mixtures experimented on, where the proportions are given, bulk, not weight, is to be understood. Many and carefully conducted experiments are needed to determine the constancy and delicacy of the reactions I have described, to say nothing of the multitude of combinations which remain untried. The subject of combinations suggests the possibility of finding certain substances which, when brought together under the influence of the fluxes, and of the different blowpipe flames, shall give decisive evidence of the presence of one or both of them, when, perhaps, alone they would wholly have escaped detection in this method of chemical investigation, and as bearing on this point, the reactions of antimony and arsenic with oxide of copper, that of the former with iron and of alumina with lime, are especially worthy of attention.

The following extracts from Muspratt's "Chemistry, as applied to Arts and Manufactures," pages 194 and 197, Art. "Devitrified or Semi-crystallized Glass," cannot fail to be of interest in connection with the subject of crystals in blowpipe beads:—

"As excessive brittleness results from the sudden cooling of glass, so, on the other hand, when the fused metal is cooled too slowly, the amorphous state entirely disappears, the mass assumes a crystalline structure, and other changes occur which are termed *devitrification*.

If the glass contains different bases, a partial separation takes place; the silica divides itself between the bases, and thus forms compounds of definite proportions which crystallize separately. In this case the intimate mixture of the materials which constitute the true glass is destroyed; the glass becomes *very hard, fibrous, opaque, much less fusible, a better conductor of heat and electricity.*"

" 'To sum up,' in the words of Dumas, to whom the editor is chiefly indebted for what has been said on this interesting subject, '*devitrification is a crystallization of glass, due to the formation of definite compounds infusible at the temperature existing at the instant of devitrification.* Sometimes this infusibility is produced by the volatilization of the alkaline base; sometimes by a single division or separation, the alkali then passing into that portion of the glass which preserves the vitreous state. All glasses may therefore be devitrified, for all glasses are capable of passing to the state of definite, and consequently crystallizable, silicates. Glasses which contain at the same time indifferent oxides and basic oxides will devitrify better than others, by the tendency which the indifferent silicates and basic silicates have to combine in definite proportions. Lastly, devitrified glasses will possess very variable properties, for their composition itself will differ completely, according to the nature of the glasses and the circumstances of devitrification. Thus sometimes the devitrified glass will be crystallized in needles of considerable size, as happens with window-glass; sometimes it will be crystallized in very fine needles, or even simply transformed into an opaline mass, without appearance of crystals, as in the case of bottle-glass.' "

#### SUPPLEMENT.

Since the preceding pages were prepared for publication, I have been enabled, through the kindness of Dr. Gibbs and Prof. Cooke, to submit Niobic Acid, Selenium, Tellurium, and Protoxide of Cerium to the methods of blowpipe examination, of which I have just treated, and with the following results.

*Niobic Acid.*—Niobic Acid ( $\text{Nb}_2 \text{O}_5$ ), with borax, after fusion in the outer flame, gives easily, either in the intermittent or fine-pointed reducing flame, a whitish precipitate, tinged with blue, yellow, and violet, and remarkably iridescent by transmitted as well as by reflected light. I have observed no crystals in this precipitate; but highly magnified, it is resolved into minute spheroidal-shaped masses. The precipitate is the same in the reducing as in the intermittent flame, and

is liable to be confounded with that given by titanitic acid when treated with the intermittent flame, unless submitted to microscopic examination, when it is easily distinguished, the titanitic acid precipitate being amorphous matter, sometimes presenting a reticulated structure, but never, to the extent of my observation, either in numerous distinct points or spheroidal.

When a small proportion of tungstic acid is present, both it and niobic can easily be distinguished, though in this case the *reducing* flame sometimes produces an amorphous precipitate not unlike that of titanitic acid, but subsequent treatment with the *intermittent* flame will bring out the characteristic spheroids of niobic acid.

Mixed with titanitic acid, niobic acid being in excess, the precipitate shows traces of the presence of the former acid; but the reaction is not nearly so definite or delicate as that just described with tungstic acid.

Manganese seems to facilitate the precipitation of niobic acid.

Columbite, from Middletown, Connecticut, gives the niobic acid precipitate, though the presence of iron detracts from its iridescence as viewed by transmitted light.

With microcosmic salt, there is a slight amorphous, brownish-yellow precipitate.

*Selenium*. — Fused with borax in the outer flame; the selenium glass, when very slightly touched with the reducing flame, gives minute, transparent, spindle-shaped crystals, forming apparently a crust on the surface of the bead. These crystals closely resemble those of selenious acid formed when selenium is heated in the closed tube.

With microcosmic salt I have obtained no reaction, the glass being exceedingly fusible.

*Tellurium*. — Its reaction is like that of selenium, except that with microcosmic salt I have observed crystals similar to those obtained with borax.

*Protoxide of Cerium*. — With borax, both in the reducing and intermittent flames, I have noticed a granular, crystalline precipitate. The crystals are very minute, and with the microscopic facilities at my disposal, I have not been able to determine their form, though of their *crystalline* character I think there can be no doubt, except in cases where the reheating process has been too much prolonged, when they appear to lose their angular structure, and sometimes fuse together to a mass not unlike the precipitate of titanitic acid in the reducing flame.

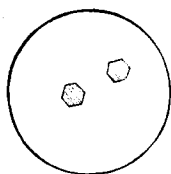


Fig. 1. Ba O.

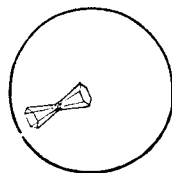


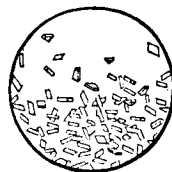
Fig. 2. Ba O.



Fig. 3. Sr O.



Fig. 4. Mg O.

Fig. 5. W O<sub>3</sub>.Fig. 6. Mo O<sub>3</sub>.

*Explanation of the Figures.*

Fig. 1. Baryta in microcosmic salt (obtained without flaming).

" 2. Baryta in borax.

" 3. Strontia in microcosmic salt.

" 4. Magnesia in borax.

" 5. Tungstic Acid in borax.

" 6. Molybdic Acid in borax.